Phase Equilibria in Materials (Nature and Phase Properties of Material-II)
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Lecture - 17
Phase Rule

It is a ~~-~~n~~N~~ew lecture on P~~p~~hase E~~e~~quilibria which is lecture number 17. So, we will just do a brief recap of~~.~~ what we have done in past couple of lectures.

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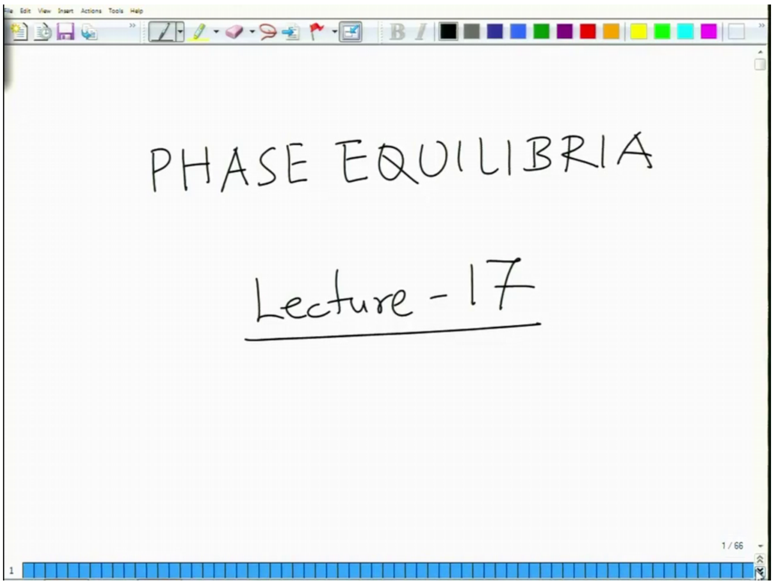

PHASE EQUILIBRIA

Lecture - 17

~~What we have done in past couple of lectures so,.~~

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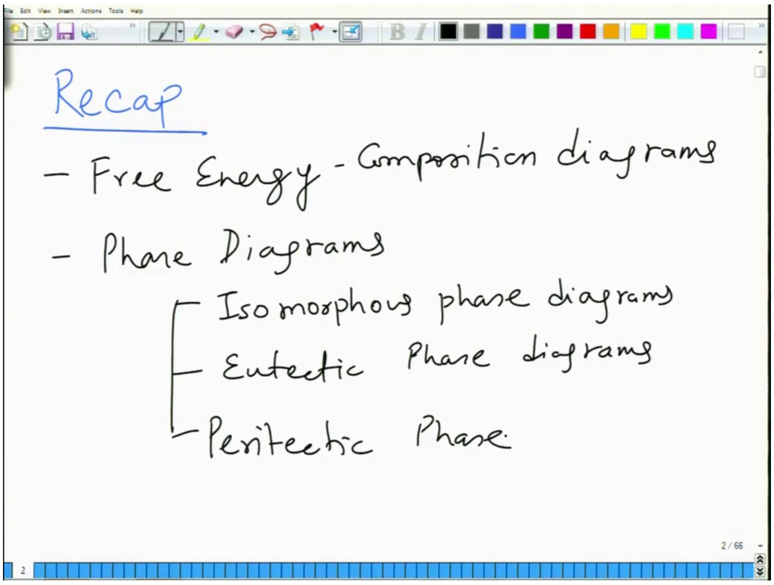

Recap

- Free Energy - Composition diagrams
- Phase Diagrams
  - Isomorphous phase diagrams
  - Eutectic Phase diagrams
  - Peritectic Phase

So, in past couple of lectures we saw free energy versus composition diagrams. So, free energy composition diagrams basically are other diagrams in which you plot the free energy of various phases at a constant temperature as a function of composition. And when you vary the temperature and look at the variation in these curves the relatively the related movement of energy composition curves of different phases, they define the new equilibrium for phase for existence of phases.

So, free energy composition phases if you vary them at various temperatures you can construct phase diagrams from them. And depending upon the type of system that you have whether you have complete miscibility of A and B in each other or they are partially miscible in each other or they are. So, or they have a immiscibility and so, on and so, forth.

So, you can draw things like you can have isomorphous phase diagram, isomorphous phase diagrams for the ones where A and B were completely a miscible in each other in both liquid and solid states, which basically meant that delta h of mixing was very low and A and B liked each other's company.

And then we had case of a eutectic phase diagram and the eutectic phase diagram typically A and B are partially miscible into each other, which means there is certain amount of solid solubility of being A and A and B. And that is because they have certain size, differences, they have differences in structure and valances.

As a difference, as a result they make a solid phase diagram in which you have 2 terminal solid solutions A and B and then you have in the intermediate region. Liquid has a minimum melting point at a temperature called as eutectic temperature and at that eutectic composition liquid completely transforms into a mixture of solid. And then we looked at another one called as peritectic phase diagram and in addition there were some other phase diagrams that we discussed.

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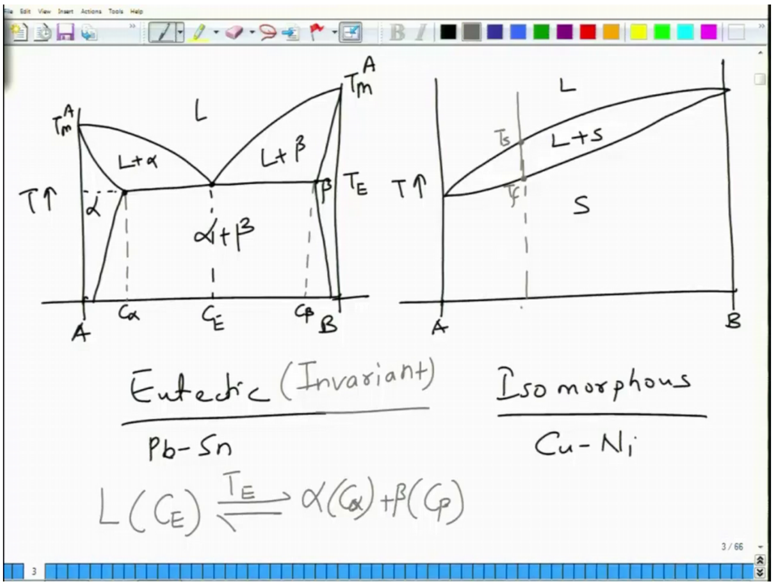

$$L(C_E) \underset{}{\overset{T_E}{\rightleftharpoons}} \alpha(C_\alpha)+\beta(C_\beta)$$

So, for example, eutectic phase diagram is something like this. So, if you draw between for A and B as a function of temperature then there is the kind of diagram you get for eutectics.

So, this is liquid, this is liquid plus alpha phase, this is alpha phase, this is beta phase region, liquid plus beta and then what you have is alpha plus beta phase region here. So, so, this is basically a eutectic phase diagram, where A and B do not have large difference in the melting points. They have they have partial solid solubility for each other in the in the solid in liquid phase and this is constructed by looking at the free energy composition diagrams at various temperatures.

Then we have another case of phase diagram called as isomorphous phase diagram. So, iso this is the isomorphous phase diagram in which you have liquid region, then you have liquid solid and then you have solid. So, solid and liquid so, A and B are miscible into each other across the whole composition range and then we had another case of. So, this is isomorphous and then we had another case of peritectic phase diagram.

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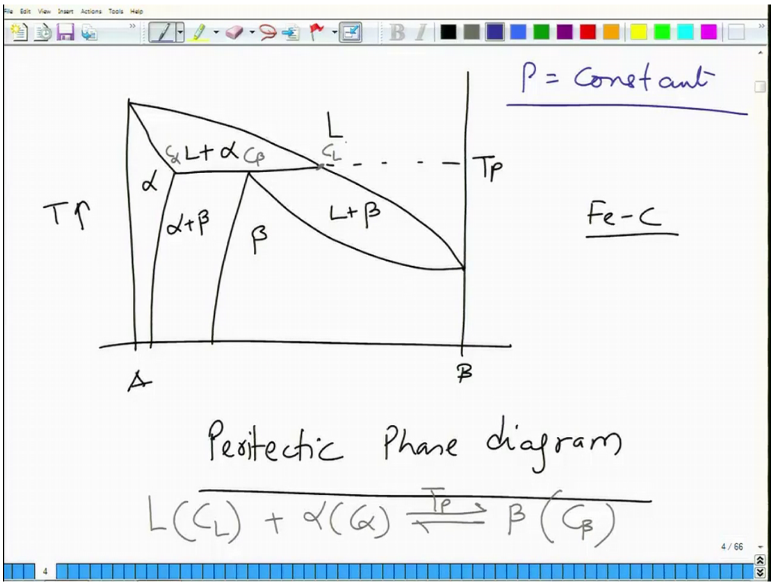

P = Constant

Fe - C

Peritectic Phase diagram

$$L(C_L) + \alpha(C_\alpha) \underset{\leftarrow}{\xrightarrow{T_P}} \beta(C_\beta)$$

Oops, this is basically a straight line let me just redraw it and then we have you can have. So, this is temperature and so, this could be liquid all across. So, let us say this is liquid plus alpha, this is alpha region this is. So, liquid plus alpha give rise to a beta phase. So, this is alpha plus beta region and then you have liquid plus beta region. So, this is the peritectic temperature at which the peritectic reaction happens. So, this is a peritectic phase diagram.

So, eutectic example could be the very common example is led, tin and isomorphous is let us say copper, nickel. Peritectic you see one portion for example, in iron carbon on the top, then you can have several other systems you also see this in various other system. We will see some examples later on of these common alloy systems which so show various kinds of phase diagrams.

So, so, all these in the 2 places at least you see that the liquid has a minimum melting point which is lower than there is a melting point which is lower than the melting point of A or melting point of B and this is called as in this case the eutectic temperature ok. So, T E, so, at this eutectic temperature liquid of compositions C E transforms into alpha and beta phase, whose composition is given by this point and this point.

So, this is C alpha and this is C beta. So, basically you can say liquid of composition C E transforms at T E to alpha of composition C alpha plus beta of composition C beta. This is the eutectic reaction which one writes. And these are called as so, this is called as an invariant reaction we will see the meaning of invariant a little later ok.

In isomorphous phase diagram basically liquid transforms into liquid plus solid. So, solid starts reappearing at this point, the transformation is complete at this point. So, this is T start this is T finish between T S and T F for a given composition you have liquid plus solid region.

This is a peritectic reaction in which at peritectic temperature liquid of composition C, CL, solid of composition C alpha. So, liquid of composition CL and solid of composition C alpha give rise to so, this is a temperature T P. They give rise to A beta phase of composition C beta. One thing that you must notice that the composition of beta phase here is intermediate between the liquid and solid composition~~.~~ ~~W~~whereas, in case of eutectic reaction the liquid composition is intermediate between alpha and beta phase compositions. So, this is the important distinction that you must draw between the 2 phase reactions.

And then there were 2 other phase reactions that we talked about.

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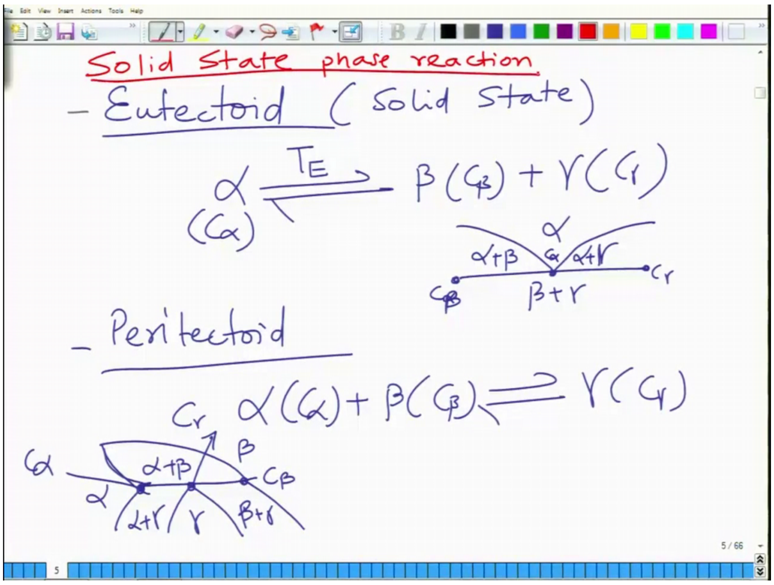

Solid State phase reaction

- Eutectoid (Solid State)

$$\underset{(C_\alpha)}{\alpha} \overset{T_E}{\rightleftharpoons} \beta(C_\beta) + \gamma(C_\gamma)$$

- Peritectoid

$$\alpha(C_\alpha) + \beta(C_\beta) \rightleftharpoons \gamma(C_\gamma)$$

One was eutectoid, eutectoid reaction is analogous to eutectic reaction where one alpha phase at eutectoid temperature of composition C alpha transforms into 2 phases C beta of compositions. So, these are all solid phases so, this is basically solid state.

So; obviously, it is a it is a part of a phase diagram it does not make a phase diagram complete by itself because it is only a solid state reaction and then we had peritectoid. And the peritectoid reaction alpha of compositions all C alpha plus beta of composition C beta transform and give rise to gamma of composition C gamma. So, this reaction is depicted in this fashion. So, you have alpha giving rise to beta plus gamma.

So, this is alpha plus beta and here you have alpha plus gamma and the compositions of beta and gamma fill this is C alpha this is C gamma and this is C beta and this reaction is basically similar to peritectic reaction ok.

So, you have you have alpha plus beta, this is alpha, this is beta phase field giving rise to gamma and this is alpha plus gamma this is beta plus gamma. So, these are the 3 composition points, this is C beta, this is the alpha and this is sorry and this is C gamma ok. So, these 2 are solid state reactions. So, they are not there are 2, 3 more phase reactions such as monotectic, syntactic etcetera, but we will we will not discuss them because beyond the purview of this course as such.

Now, what we will do is that what we have looked at is how to draw the phase diagram, what kind of phase reactions are there depending upon the time, defining the type of phase diagram. Now, what we will do is that now we will see that what is the correlation between.

So, in a phase diagram what you see is that. So, if you look at a phase diagram for instance this phase diagram. In a phase diagram you see that ~~the~~ if the pressure is constant, if P is constant then we have 2 variables here, one is a temperature, second is the composition. So, as a function of composition and temperature what kind of phases exist? How many independent variables that we have at a given set of condition at a given point in the phase diagram? That is something which has to be determine.

So, basically this is so, we can see that if you want to determine the number of phases at under given certain of a given set of conditions or we want to determine what kind of parameters, we can change for a given type of phases. And for a given composition and temperature and, temperature could be a variable composition could be variable.

So, whether they are independent variable or whether they are dependent variable that needs to be determine for a given that that is something that we can know about from the phase diagram. So, basically we want to understand what is the effect of change in the variables on the phase stability and alternatively what kind of independent variables that we can have given certain scenario is.

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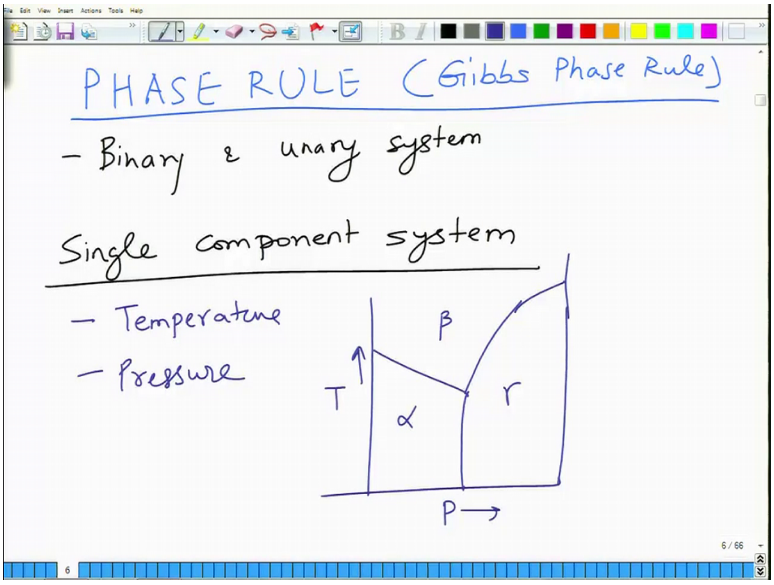

PHASE RULE (Gibbs Phase Rule)

- Binary & unary system

Single component system

- Temperature
- Pressure

So, this is plane by a concept called as phase rule. S~~s~~ome people also called as Gibbs phase rule, but in general it is known as phase rule and here we are limited to binary system mainly. Binary and perhaps unary systems, but it is possible to extend this into other systems as well.

So, in a 2 phase so, in a ~~in a~~ single phase component in a single component system. So, in a single component system let us say the variables that we had were we had temperature and we had pressure. Because, there is single component so, it would be, it would be interesting to see what kind of phases will exist when you vary temperature or pressure or both and in what region because how does this vary as a function of.

So, for example, if you have a phase diagram like this let us say something like that let us say. So, you have let us say alpha phase, you have beta phase, you have gamma phase and this is let us say temperature and this is pressure what kind of phases exist under radius set of conditions. So, that we can see with the help of this phase rule, you can have 2 phase equilibrium for instance.

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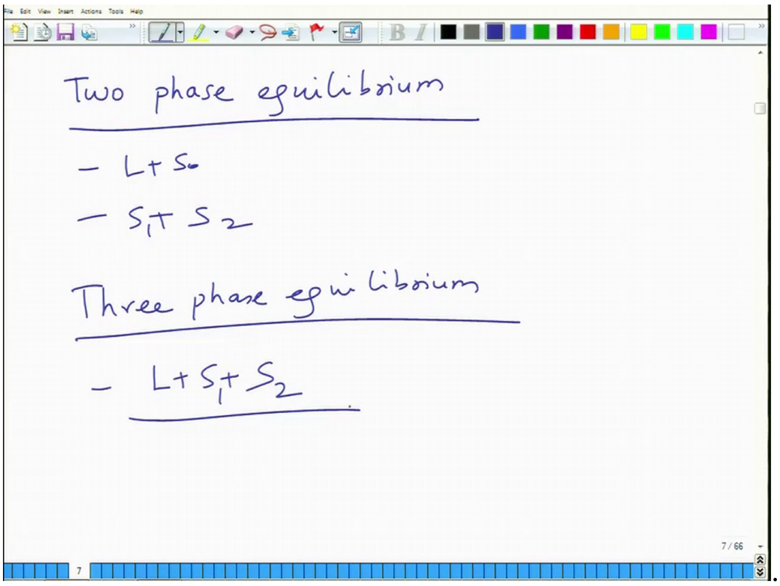

Two phase equilibrium

- $L + S$
- $S_1 + S_2$

Three phase equilibrium

- $L + S_1 + S_2$

As we have seen in binary systems you can have liquid plus solid, you can have solid plus solid and so, on and so, forth.

You can have 3 phase equilibrium, this could be you know liquid plus solid plus solid for instance in eutectic phase diagram and so, on and so, forth. So, so, generally what we see is that if you look at the phase diagram generally.

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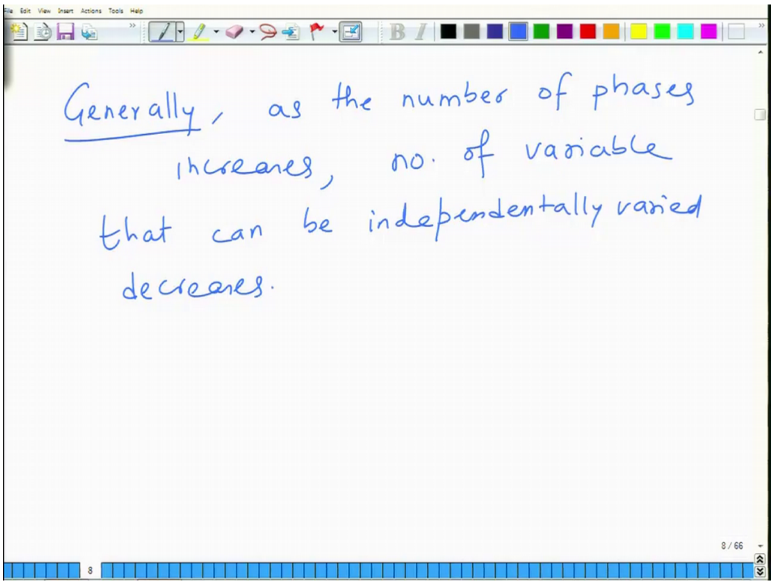

Generally, as the number of phases increases, no. of variable that can be independentally varied decreases.

As the number of so, if you study you know single component phase diagrams and 2 component binary systems, there is a there is a conclusion that you draw that as a number of phases increases, a number of variables that can be independently varied decreases. This is something that we generally observed from phase diagram.

So, you can see that in case of single component system, when you have single phase regions you can vary both temperature and pressure. But, when you do binary system there are certain regions where you can vary only one component. We will see the other parameter is fixed and there are certain cases where there is no change in parameter what is over. So, as we will see in biodefense diagrams for example, if you have a 3 phase coexistence you will see that those points are invariant.

So, generally a 2 phase region is called as an area connecting single when you have 2 phase coexistence, it is like it is a line it is a one-dimensional change in the parameter. When you have 3 phase coexistence it is like a point and when you have so, 0 D when you have a single phase coexistence then it is like a area, you can vary both the parameters. So, we will see that distinction between the 3 in the coming few minutes.

So, let us see so, to begin with how to correlate.

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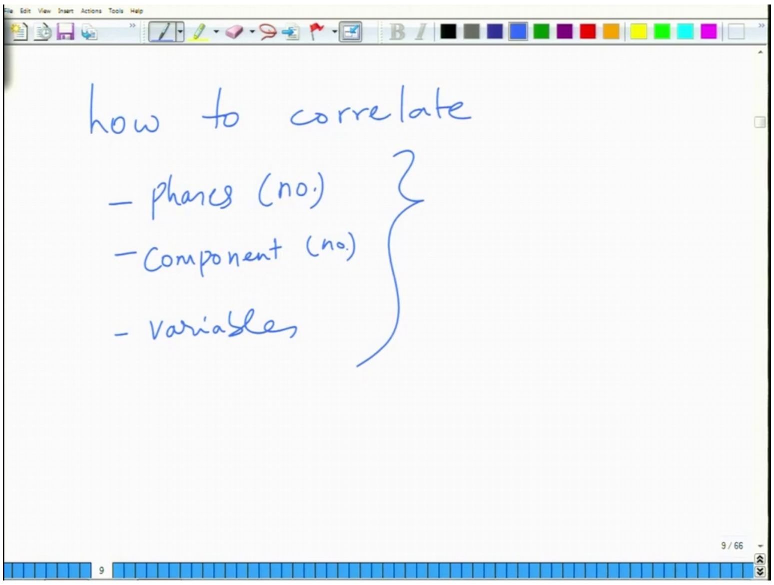

how to correlate

- phases (no.)
- Component (no.)
- variables

So, we can say how to correlate phase's number, components, that is independent species and variables for a given system. This is the objective of phase rule, how to correlate the number of phases, number of components in a given system and number of variables that are available to you to vary independently in a given system to predict the phase equilibrium. This is the objective of phase rule.

~~So, to begin with let us first if you have.~~

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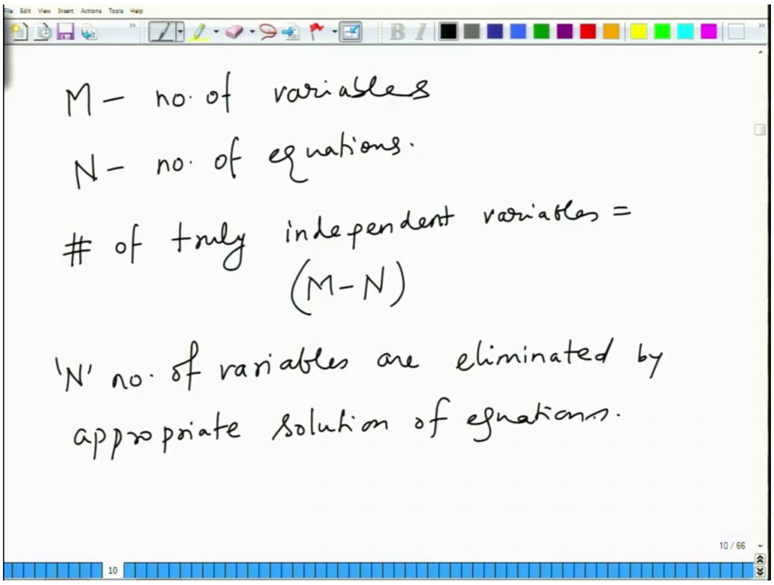

M – no. of variables

N – no. of equations.

$\#$ of truly independent variables = $(M-N)$

'N' no. of variables are eliminated by appropriate solution of equations.

So, to begin with let us first if you have let us say M number of variables, so, you have M number of variables, these M number of variables are related by N number of equations. So, truly independent variables are only so, number of are given by M minus N. So, basically M has to be larger than N.

So, basically what it means is that out of these total number of variables, M number of variables are eliminated by appropriate solution of equations. So, basically what you have is if you have M number of variables and number of equations where M is larger than N, the number of truly independent variables has M minus N. What it means is that that out of this M, N number of variables are eliminated by appropriate solutions of equations and basically they are not dependent, they are not independent variables.

So, let me give you an example so, if you have for example, here by this definition if you have M is equal to N. It means that you have a unique solution available for a given set of equations.

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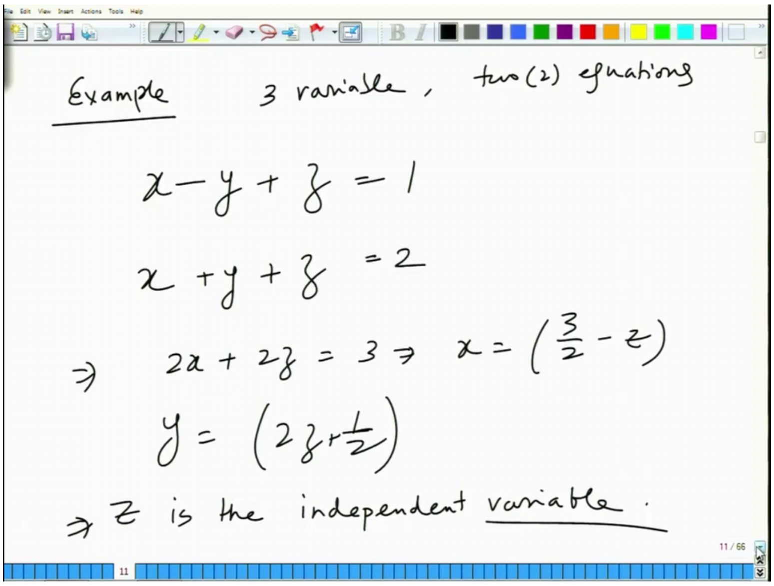

Example 3 variable , two (2) equations

$$x - y + z = 1$$

$$x + y + z = 2$$

$$\Rightarrow 2x + 2z = 3 \Rightarrow x = \left(\frac{3}{2} - z\right)$$

$$y = \left(2z + \frac{1}{2}\right)$$

$\Rightarrow$ z is the independent variable.

So, let us take an example.

So, we have 3 variables and 2 equations. So, the first one is x minus y plus z is equal to 1 and second one is x plus y plus z is equal to 2. So, we can see that we have 3 variables and 2 equations.

Now we can rewrite these equations as. So, if you just rearrange you get 2 x plus 2 z is equal to 3. What it means is that you have x is equal to 3 by 2 minus z and then you can substitute in one of these equations to get y and this y turns out to be 2 z plus 2 by 2. So, you can see that right the only independent variable out of these 3 variables is z, that is only one variables.

In this case you can see that z is the independent. So, by choosing a value of z you can define both x and y for these 3. So, this is the basically summary of what I said in the earlier slide.

Now, put it in put a put this in context of thermodynamic variables.

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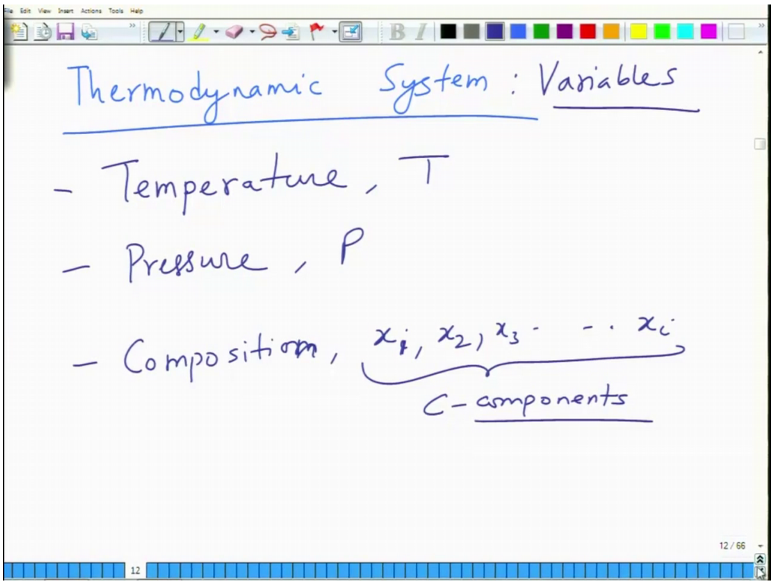

Thermodynamic System : Variables

- Temperature, T
- Pressure, P
- Composition, $\underbrace{x_1, x_2, x_3 \cdots x_c}_{C-\text{components}}$

So, now let us go back to thermodynamic system. So, basically it is a material where temperature is a variable, pressure is a variable and then you have composition. So, if it is a multi-component system then it is you can have composition starting from x I basically x 1, x 2, x 3 and so, on and so, forth. Let us say total number of components is equal to what this means is that you have C components. So, you have C number of components for a given system.

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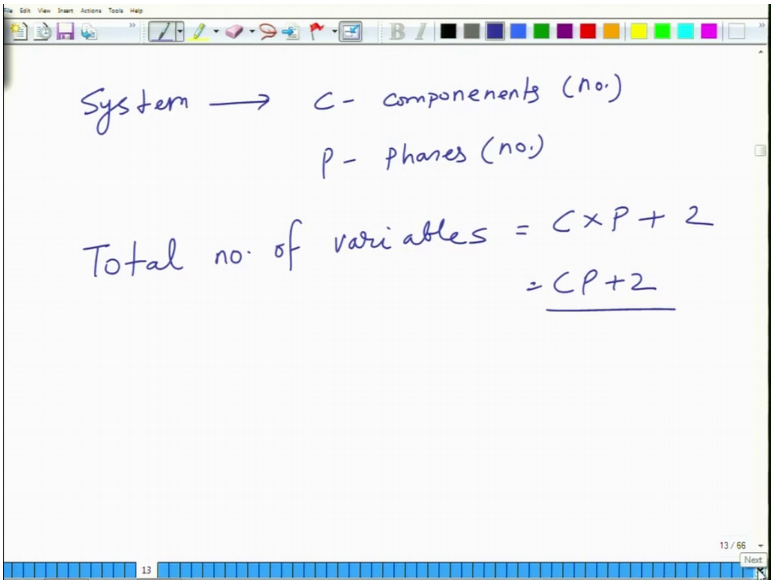

System $\rightarrow$ C - components (no.)

P - phases (no.)

Total no. of variables $= C \times P + 2$

$= CP + 2$

So, system has C components and these C components give rise to P number of phases. So, this is number of phases and this is C number of components both are number. So, total number of what is total number of variables? Total number of variables is C multiplied by P. So, you have C components, P phases. So, for each phase you will have one of them. So, you multiplied C with P so each phase will have C variables. So, C into P total number of variables plus temperature and pressure. So, you have CP plus T is the CP plus 2 is the total number of variables and this 2 comes from temperature and pressure.

So, now let us see how do we look at this in the context of phase equilibria.

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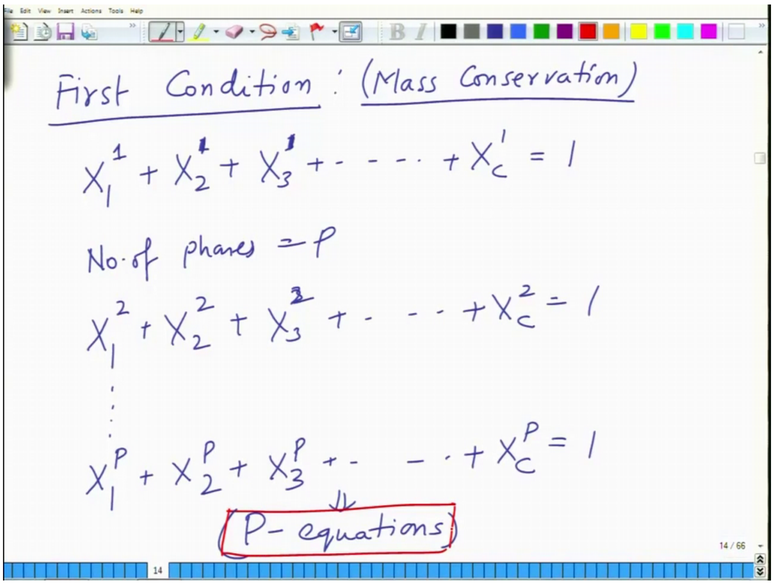

First Condition : (Mass Conservation)

$X_1^1 + X_2^1 + X_3^1 + \cdots + X_C^1 = 1$

No. of phases = P

$X_1^2 + X_2^2 + X_3^2 + \cdots + X_C^2 = 1$

$\vdots$

$X_1^P + X_2^P + X_3^P + \cdots + X_C^P = 1$

$\downarrow$

$\boxed{\text{P- equations}}$

So, the first condition for a given alloy system comes from basically mass conservation. Because, whatever you do your mass in a mass of all the elements in a given system is conserved. So, which means that X 1 in phase 1 plus X 2 in phase 2 plus X 3 in phase 3 and XC in phase 1 sorry,~~.~~ ~~T~~this is phase 1 not phase 3.

So, in 1 phase, in phase 1 X of all the elements the weight of all the elements is mole fraction of all the element weight fraction of all the elements is equal to 1. So, sum of more fractions of all the components in a single phase is equal to 1 and if you have number of phases as P as we defined earlier we can write this as X 1 2 for the second phase. And if you keep writing this for number of phases then you can say that this is X 1 P plus X 2 P plus X 3 P plus X C P is equal to 1.

So, how many equations will this give rise to? This will give rise to P equations. So, total number of equations that you obtain out of this will be equal to P set of equations.

~~Now, the second condition is.~~

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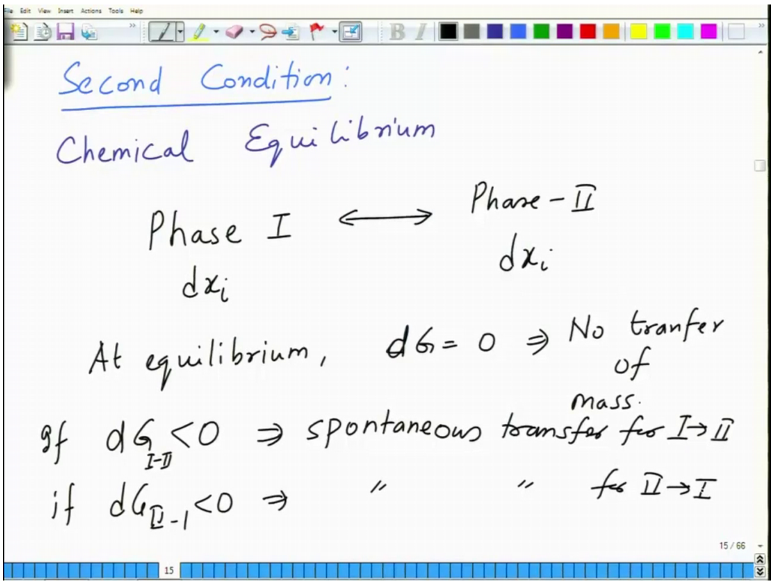

Second Condition:

Chemical Equilibrium

Phase I $\longleftrightarrow$ Phase-II

dx_i dx_i

At equilibrium, $dG = 0 \Rightarrow$ No tranfer of mass.

If $dG_{I-II} < 0 \Rightarrow$ spontaneous transfer for $I \rightarrow II$

if $dG_{II-I} < 0 \Rightarrow$ " " for $II \rightarrow I$

Now, the second condition is s~~S~~econd condition comes from chemical equilibrium. Now, chemical equilibrium says that so~~,~~ if you have let us say phase 1 and let us say you take for a particular element dx i and you transfer this to phase 2. So, there is a transfer of mass between 2 phases, let us say and you add here dx i. At equilibrium if the equilibrium is maintained then delta G is equal to 0 which means at.

So, let us say dG is equal to 0, what it means is that basically no transfer of mass ok. So, for mass transfer to happen so, if let us say we are considering the transfer from 1 to 2. So, if dG for this process is less than 0 which means it is spontaneous 1 to 2. So, dG 1 to 2 or if dG 2 to 1 is less than 0 then you have a spontaneous transfer for 2 to 1 ok. So, this is the free energy change that you are going to happen.

Now, free energy will change the total free energy will change as you as you change the mass from one face to another you have some changes in the free energy. So, if let us say.

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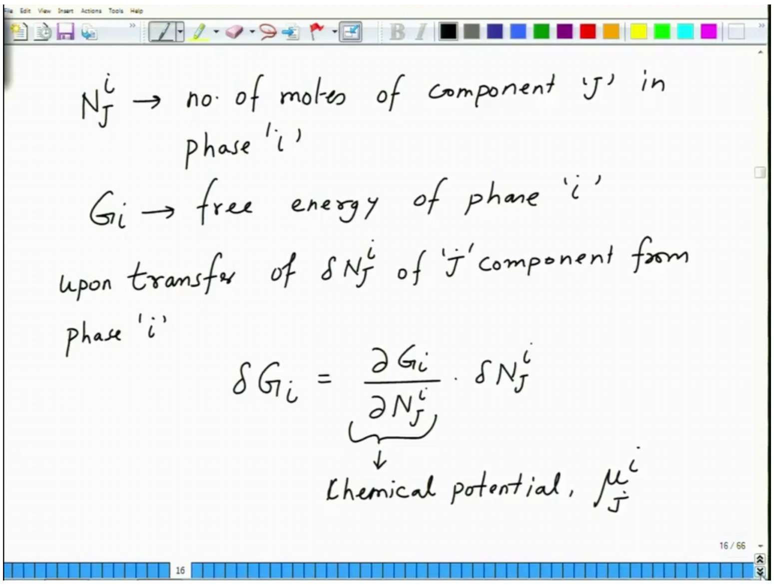

N_J^i → no. of moles of component 'J' in phase 'i'

G_i → free energy of phase 'i'

upon transfer of δN_J^i of 'J' component from phase 'i'

$$\delta G_i = \underbrace{\frac{\partial G_i}{\partial N_J^i}}_{\downarrow \text{ Chemical potential, } \mu_J^i} \cdot \delta N_J^i$$

If N j i is the number of moles of component let us say j ~~eth~~ th in phase i ok. So, it is i ~~eth~~ th phase and j ~~eth~~ th component and let us say G i is the free energy of. So, we are saying that it is phase i ok. So, free energy of phase i is G i and N j i is the number of moles of component j in phase i.

So, let us say the transfer happens so, upon transfer of del j del N j i. So, very small amount of j ~~eth~~ th component from i phase to another phase ok. So, upon transfer of del N j i of j component from phase i. So, let us so I write change in the free energy let us say. I can write delta Gi is equal to del Gi divided by del N j i into delta N j i.

So, this is the incremental change in the free energy of i ~~eth~~ th phase upon causing a incremental change in the composition of component j. So, this is basically the, if you recall this is called as chemical potential. So, basically this is mu j in i ~~eth~~ th phase. So, ~~so~~ chemical potential of jth ~~eth~~ component in ith ~~eth~~ phase.

So, now how will this affect the other phase? ~~So, this amount goes to.~~

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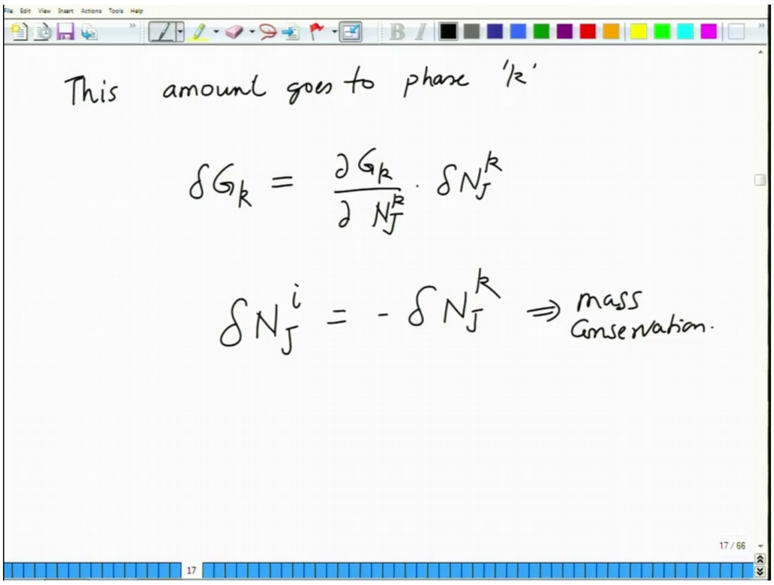
This amount goes to phase 'k'

$$\delta G_k = \frac{\partial G_k}{\partial N_J^k} \cdot \delta N_J^k$$

$$\delta N_J^i = - \delta N_J^k \Rightarrow \text{mass Conservation.}$$

So, this amount goes to i~~I~~t goes to phase k. S~~s~~o, changes in it is free energies for k~~ eth ~~th phase. So, delta G, then delta G k is equal to del G k divided by del of N j k into delta N j k. So, this is the free energy change that happens when the element has entered into phase k, but the amount of solute that has entered the phase k is same as the amount of solute that has left phase i. Which means del N j i is equal to minus of del N j k because the mass is conserved. So, this is mass conservation.

So, now, what we will do is that we do not have time now for doing this, but what we will do is that we will now take this further to establish the free energy condition. T~~t~~hat is the free total free energy change for the system to equilibrium must be equal to 0. So, if that happens then what is the condition at which we arrive, ok. So, we will do that in the next class.

What we are have we have done in this class is we are basically started the procedure for establishing the phase rule conditions basically, to find out the phase equilibrium in terms of number of phases, number of components and number of content components with the number of independent variables that are available. And to find to correlate them to find the phase called equilibrium so, we will further dwell on this in the next class.

Thank you.